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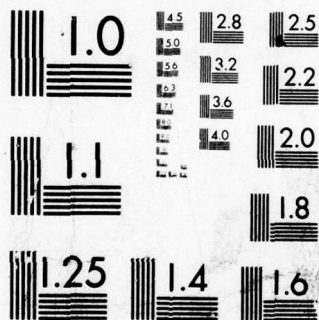
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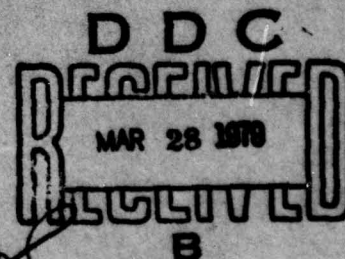
Rate Coefficients Calculated by the Bond-Energy  
Bond-Order Method for Excited-State  
 $F + H_2 \rightleftharpoons H + HF$  Reactions

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16 February 1979

Interim Report

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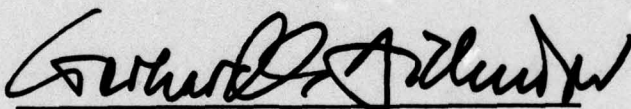
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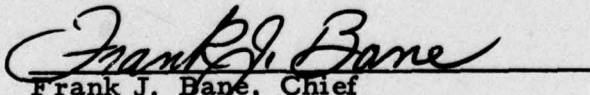
This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



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Project Officer

FOR THE COMMANDER



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Because of the importance of rate coefficients in determining the power output of HF and DF chemical lasers, the bond-energy bond-order (BEBO) method for predicting rate coefficients is applied herein to the excited-state reactions $H_2^n(y \text{ kcal}) + F \rightleftharpoons H + HF(v = 0, 1, 2, 3, \dots)$ and $D_2^n(y \text{ kcal}) + F \rightleftharpoons D + DF(v = 0, 1, 2, 3, \dots)$ $\rightarrow$ next page <i>in equilibrium with</i>		

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19. KEY WORDS (Continued)

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where the value of  $y$  is 0, 1, 2, 4, 8, . . . , kcal of excitation. Inversions for these chemical laser reactions are predicted with this method inasmuch as the computed rate coefficients for the production of vibrationally excited HF and DF are higher than for ground-state HF and DF. Good agreement is obtained between computed and measured rate coefficients for the reaction of  $H_2^v$  and  $D_2^v$  with F atoms. The calculations also indicate that excitation of the  $H_2^v$  and  $D_2^v$  reactants can enhance the HF and DF inversions. An analysis is made to determine the molecular properties responsible for the larger rate coefficient for the formation of excited HF, and the vibrational frequencies are shown to be significant factors. The computations represent the first application of the BEBO method for calculating rate coefficients for the production of excited states.

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## PREFACE

We wish to thank Professor Robert W. Carr of the University of Minnesota for sending a copy of his BEBO computer program. The excellent assistance of Mrs. Karen Foster in improving the computer program is gratefully acknowledged.

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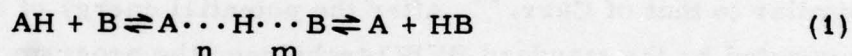
## I. INTRODUCTION

The kinetics of fluorine atom reactions with  $H_2$  or  $D_2$  to produce vibrationally excited HF or DF molecules has been of significant interest during recent years because of their importance in high-power chemical lasers.<sup>1-3</sup> The attainment of larger rates for the formation of vibrationally excited HF or DF reaction products than for HF( $v = 0$ ) or DF( $v = 0$ ) is a goal in designing and operating such chemical lasers because excited-state inversion is the basis for obtaining lasing power. A bond-energy bond-order (BEBO) method for predicting the rate coefficients and activation energies of ground-state hydrogen transfer reactions in the gas phase was developed and tested by Johnston and others.<sup>4-7</sup> These predictions provided satisfactory agreement with experimental rate coefficients for many ground-state hydrogen transfer reactions. The BEBO method, however, has not hitherto been applied and tested for excited-state reactions. Consequently, this work was undertaken in order to examine the applicability of the method for predicting inversions for chemical-laser reactions in which the HF or DF products are excited and in which the  $H_2$  or  $D_2$  reactants are in the ground or excited state.

## II. COMPUTATION METHOD FOR EXCITED STATES

The BEBO method was developed<sup>4, 5</sup> to provide a convenient, rapid technique for obtaining approximate predictions of rate coefficients and activation energies on the basis of known molecular parameters, such as bond dissociation energies, bond lengths, and vibration frequencies. The method is based on the principles of small vibration dynamics in molecules and on transition-state theory. No adjustable parameters are required with this method and it is much briefer computationally than *ab initio* quantum mechanical methods<sup>8</sup> or the London-Eyring-Polanyi-Sato (LEPS) transition state method, which requires calculations for a relatively large potential energy surface.<sup>9, 10</sup>

The BEBO method is based on a model of the hydrogen transfer reaction



in which the sum of the bond order  $m$  of the new bond and the bond order  $n$  of the breaking bond is equal to one.<sup>5</sup> In this model of the simultaneous formation of the  $\text{H} \cdots \text{B}$  bond and the breaking of the  $\text{A} \cdots \text{H}$  bond, it is assumed that the energy that is being released during formation of the new bond can be used to supply part or all of the energy required for breaking the  $\text{A} \cdots \text{H}$  bond. If the energy needed in dissociating the  $\text{A} \cdots \text{H}$  bond is greater than the energy available from the  $\text{B} \cdots \text{H}$  bond during its formation, this difference is computed as the potential energy of activation. The computer program calculates this difference on the basis of the following related trial assumptions incorporated into the BEBO method:

1. The Pauling rule<sup>11</sup> for the relationship between bond length and bond order applies in the transition state.
2. The Lennard-Jones 6-12 energy and distance parameters<sup>12</sup> for the noble gases represent the zero-order bond energies and internuclear distances for elements in the corresponding row of the periodic table.

3. The triplet repulsion that results from uncoupled spins is represented by a Sato<sup>9</sup> anti-Morse function similar to that for the triplet  $^3\Sigma_u^+$  state of  $H_2$ .
4. The logarithm of bond energy is proportional to the logarithm of bond order.<sup>4, 5</sup>

These trial assumptions have provided satisfactory agreement between computed and experimental rate coefficients and activation energies for several reactions.<sup>4-7, 13</sup> Nevertheless, it must be cautioned that such assumptions are primarily empirical, and calculations derived on the basis of these assumptions must be considered as approximations of the true kinetic parameters until proven otherwise. Additional assumptions were avoided wherever possible in this application of the BEBO method to the excited-state reactions of  $H_2$  or  $D_2$  with F atoms.

The bond dissociation energies for the excited states were obtained from Table 6 of a compilation by Cohen and Bott.<sup>14</sup> The computer program was similar to that of Carr.<sup>15</sup> After the potential energy of activation  $V^*$  was computed by the standard BEBO technique, the program then computed a pre-exponential factor B by the use of the partition functions (including the contributions of the quantum factors) calculated by the local properties formulation.<sup>4, 5, 15</sup> The rate coefficient  $k_v$  was calculated in units of cubic centimeters per mole per second.

$$k_v = B \exp(-V^*/RT) \text{cm}^3/\text{mol-sec} \quad (2)$$

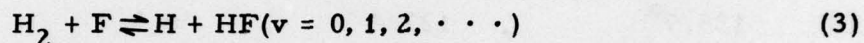
The activation energy  $E_a$  in the region of T was calculated by using the computed values of  $k_v$  at T and  $k_v$  at T - 50 K, with the assumption that  $E_a$  would not vary much with temperature in this relatively small temperature range.



### III. RESULTS AND DISCUSSION

Molecular parameters used for these computations by the BEBO method are listed in Table 1 together with the sources for these data.

A summary is presented in Table 2 of the computed BEBO values for the rate coefficients and potential energies of activation for the formation of excited HF by the reaction of F with ground-state H<sub>2</sub>



The  $k_v$  values in Table 2 indicate that the BEBO method can be used to predict inversions for H<sub>2</sub> + F chemical laser reaction inasmuch as computed rate coefficients for the production of vibrationally excited HF are higher than for ground-state HF. For example, the rate coefficient for production of HF( $v = 2$ ) is about twice that for production of ground-state HF. This result may seem somewhat unexpected because higher potential energies of activation could be anticipated for production of HF( $v = 2$ ) on the basis of the following considerations. As mentioned in Section II, the energy available from the formation of the new bond H...F can be used to supply energy required to break the old bond, H...H in this case. However, because HF( $v = 2$ ) is vibrationally excited to the extent of 23 kcal/mol, correspondingly less energy is available during the formation of HF( $v = 2$ ) to help supply the energy needed as H...H dissociates. In fact, the values of  $V^*$  in Table 2 indicate that  $V^*$  is 0.79 kcal higher for HF( $v = 2$ ) than for HF( $v = 0$ ), and that  $V^*$  for HF( $v = 3$ ) is 2.9 kcal higher than for HF( $v = 2$ ). The computed pre-exponential term  $B$  is sufficiently larger for HF( $v = 2$ ) than for HF( $v = 0$ ), which compensates for the effect of higher  $V^*$  in this case. The factors that influence the value of  $B$  as a function of the HF vibrational quantum number  $v$  are discussed in some detail later. For HF( $v = 3$ ), the computed results in Table 2 indicate that the increase in  $B$  was not sufficient to overcome the effect of the higher  $V^*$  in lowering the computed rate coefficient.



Table 1. Molecular Parameters for H<sub>2</sub>, D<sub>2</sub>, HF, and DF

	Bond Dis- sociation Energy, <sup>a</sup> kcal	Bond Dissociation Energy for First Vibrational Level, <sup>b</sup> kcal	Inter- atomic Distance, <sup>c</sup> 10 <sup>-8</sup> cm	Vibrational Wave Number, <sup>c</sup> cm <sup>-1</sup>
H <sub>2</sub>	103.2 <sup>a</sup>	91.3	0.742	4405
D <sub>2</sub>	105.0 <sup>a</sup>	96.5	0.742	3119
HF	135.1 <sup>b</sup>	123.8	0.917	4138
DF	135.7 <sup>a</sup>	127.4	0.917	2998

<sup>a</sup>B. Darwent, Bond Dissociation Energies in Simple Molecules, Report No. NSRDS-NBS 31 National Bureau of Standards, Washington D.C., (1970).

<sup>b</sup>The bond dissociation energies for the vibrational levels were obtained with the use of the energy values in Table 6 of Ref. 14.

<sup>c</sup>JANAF Thermochemical Tables, D. R. Stull and H. Prophet, 2nd ed., Report No. NSRDS-NBS 37, National Bureau of Standards (1971).

Table 2. Computed Rate Coefficients for Excited HF Formation from Ground-State H<sub>2</sub>

HF Vibrational Level	Rate Coefficient, 10 <sup>13</sup> cm <sup>3</sup> /mol-sec		Pre-exponential, 10 <sup>14</sup> cm <sup>3</sup> /mol-sec		V*, kcal/mol	Activation Energy, kcal/mol	
v	200 K	300 K	200 K	300 K		200 K	300 K
0	0.017	0.137	0.13	0.25	1.73	2.46	2.55
1	0.026	0.177	0.24	0.36	1.79	2.24	2.32
2	0.054	0.263	3.06	1.80	2.52	1.85	1.92
3	0.002	0.031	190.0	27.6	5.42	3.07	3.15

The sum of the rate coefficients at 300 K (Table 2) for the production of HF( $v = 0, 1, 2, 3$ ) from ground-state  $H_2$  is  $0.61 \times 10^{13} \text{ cm}^3/\text{mol-sec}$ . Cohen and Bott<sup>16</sup> selected  $k_3 = 2.3 \times 10^{14} \exp(-1600/RT)$  as the probable best value for the rate coefficient of reaction (3), and a value of  $1.5 \pm 0.5 \times 10^{13} \text{ cm}^3/\text{mol-sec}$  for  $k_3$  at 300 K. Consequently, the computed BEBO rate coefficient of  $0.61 \times 10^{13} \text{ cm}^3/\text{mol-sec}$  is in fair agreement with this experimental  $k_3$ . Tunneling factors were not applied in these BEBO calculations because their use did not appear justified by the expected reliability of the computed results, and because there still is considerable disagreement about the proper procedure for making tunneling corrections.<sup>4, 5, 15</sup> A tunneling correction would increase the computed BEBO rate coefficient and therefore could improve the agreement between the computed and experimental value of  $k_3$ .

The results in Table 2 indicate that the activation energy  $E_a$  decreases slightly at  $T = 200 \text{ K}$  compared with  $T = 300 \text{ K}$ . When this small dependence of  $E_a$  on  $T$  is converted into a  $T^P$  dependence in the pre-exponential,  $k_3$  can be expressed as  $10^{13.61} T^{0.11} \exp(-2235/RT) \text{ cm}^3/\text{mol-sec}$ . Experimental evidence summarized by Cohen and Bott<sup>16</sup> indicates that the rate coefficient for the production of HF( $v = 2$ ) is larger than that for HF( $v = 1$ ) or HF( $v = 3$ ). Accordingly, the corresponding BEBO  $k_v$  in Table 2 is consistent with this experimental result. However, even at 200 K, the BEBO results give  $k_{v=2} \approx 2 k_{v=1}$ , whereas the experimental observation was  $k_{v=2} > 3 k_{v=1}$ .<sup>15</sup> The BEBO  $k_v$  for production of HF( $v = 3$ ) from ground-state  $H_2$  is at least an order of magnitude smaller than for  $v = 2$ , whereas experimental results give  $k_{v=3}/k_{v=2} = 0.49$ . The BEBO computational results for the reaction involving excited  $H_2$ , however, do indicate that  $k_v$  for HF( $v = 3$ ) production increases rapidly if the  $H_2$  reactant is excited and that the computed  $k_{v=3}/k_{v=2}$  exceeds 0.5 before  $H_2$  excitation reaches 2 kcal/mol. The computed BEBO activation energy for HF( $v = 1$ ) production exceeds that for  $v = 2$  by about 400 cal/mol. This is in fair agreement with experiment.<sup>17</sup>

Scientists working with HF chemical lasers have speculated that inversion might be increased by supplying excitation to the reactant  $H_2$  or  $D_2$ . The



BEBO method was applied herein in order to examine this question. Computed results are summarized in Table 3 for reactant  $H_2$  excitations in the amounts 1, 2, 4, 8, and 11.9 kcal/mol. The last value corresponds to the first vibrational level (with no rotational excitation). The computed rate coefficients (Table 3) indicate that inversions are generally increased by excitation of the  $H_2$ , with higher  $H_2$  excitation producing larger rate coefficients for the generation of excited HF. Improved inversions resulting from  $H_2$  excitation were also reported by Coombe and Pimentel.<sup>18</sup> Because vibrational excitation decreases the energy needed to break the  $H_2$  bond, it is not surprising that potential energies of excitation decrease as  $H_2$  excitation increases (Fig. 1). This effect is more marked for the production of  $HF(v = 3)$  than for  $HF(v = 0, 1, \text{ or } 2)$  because  $V^*$  for the latter was not large even when unexcited  $H_2$  was the reactant. For 11.9 kcal/mol excitation of  $H_2$ , the computed rate coefficient of 300 K for the production of  $HF(v = 3)$  is 2.7 times that for  $HF(v = 0)$ , whereas for ground-state  $H_2$  reactant, the  $k_v$  for  $HF(v = 3)$  is only 21% of that for  $HF(v = 0)$ . Even with only 2 kcal/mol excitation of  $H_2$ ,  $k_v$  for  $HF(v = 3)$  is 1.2 times that for  $HF(v = 0)$ . Improvement in the inversions for  $HF(v = 3)$  brought about by excitation of  $H_2$  reactant may be expected to produce higher total lasing energy output because the cascading of  $HF(v = 3)$  to lower vibrational levels as lasing occurs may have the effect of successively improving inversions from the  $v = 2$  and the  $v = 1$  levels.

Figure 1 and Table 3 indicate that the rate coefficient for the production of  $HF(v = 4)$  increases rapidly when the excitation of  $H_2$  increases from 8 to 11.9 kcal/mol. Consequently, the overall rate coefficient (as shown in Fig. 1 by the curve with the closed data points) also increased rapidly for values of  $H_2$  excitation exceeding 8 kcal/mol.

The relative abundance of information on kinetic parameters (Fig. 1) for the production of  $HF(v = 1, 2, 3, \text{ and } 4)$  excited states is in marked contrast with the limited information for reaction obtained from earlier BEBO computations.<sup>4-7, 15</sup> Previously, BEBO computations have been concerned

Table 3. BEBO Rate Coefficients for Excited HF Formation from Excited H<sub>2</sub>

H <sub>2</sub> Excitation, kcal/mol	HF Vibration, v	Rate Coefficient, 10 <sup>13</sup> cm <sup>3</sup> /mol-sec		Pre-exponential, 10 <sup>14</sup> cm <sup>3</sup> /mol-sec		V*, kcal
		200 K	300 K	200 K	300 K	
1	0	0.020	0.16	0.13	0.25	1.64
1	1	0.033	0.21	0.21	0.34	1.69
1	2	0.061	0.29	1.72	1.25	2.24
1	3	0.011	0.09	195.0	28.0	4.80
2	0	0.025	0.18	0.13	0.25	1.56
2	1	0.041	0.25	0.20	0.33	1.54
2	2	0.066	0.31	1.01	0.89	2.00
2	3	0.044	0.22	176.0	26.0	4.21
4	0	0.036	0.24	0.13	0.26	1.41
4	1	0.063	0.34	0.18	0.32	1.33
4	2	0.099	0.43	0.54	0.61	1.59
4	3	0.290	0.79	86.0	16.0	3.18
4	4	0.000	0.00	1.9	1.3	8.33
8	0	0.069	0.39	0.13	0.27	1.17
8	1	0.136	0.61	0.17	0.33	1.01
8	2	0.197	0.75	0.26	0.41	1.02
8	3	0.657	1.43	4.19	2.29	1.65
8	4	0.000	0.26	4.84	2.69	4.84
11.9 <sup>a</sup>	0	0.12	0.58	0.14	0.30	0.99
11.9	1	0.26	1.10	0.20	0.38	0.80
11.9	2	0.41	1.34	0.24	0.43	0.69
11.9	3	0.63	1.57	0.51	0.63	0.83
11.9	4	3.79	4.49	245.0	34.0	2.57
11.9	5	0.00	0.00	3.8	2.9	8.87

<sup>a</sup>First vibrational level of H<sub>2</sub>



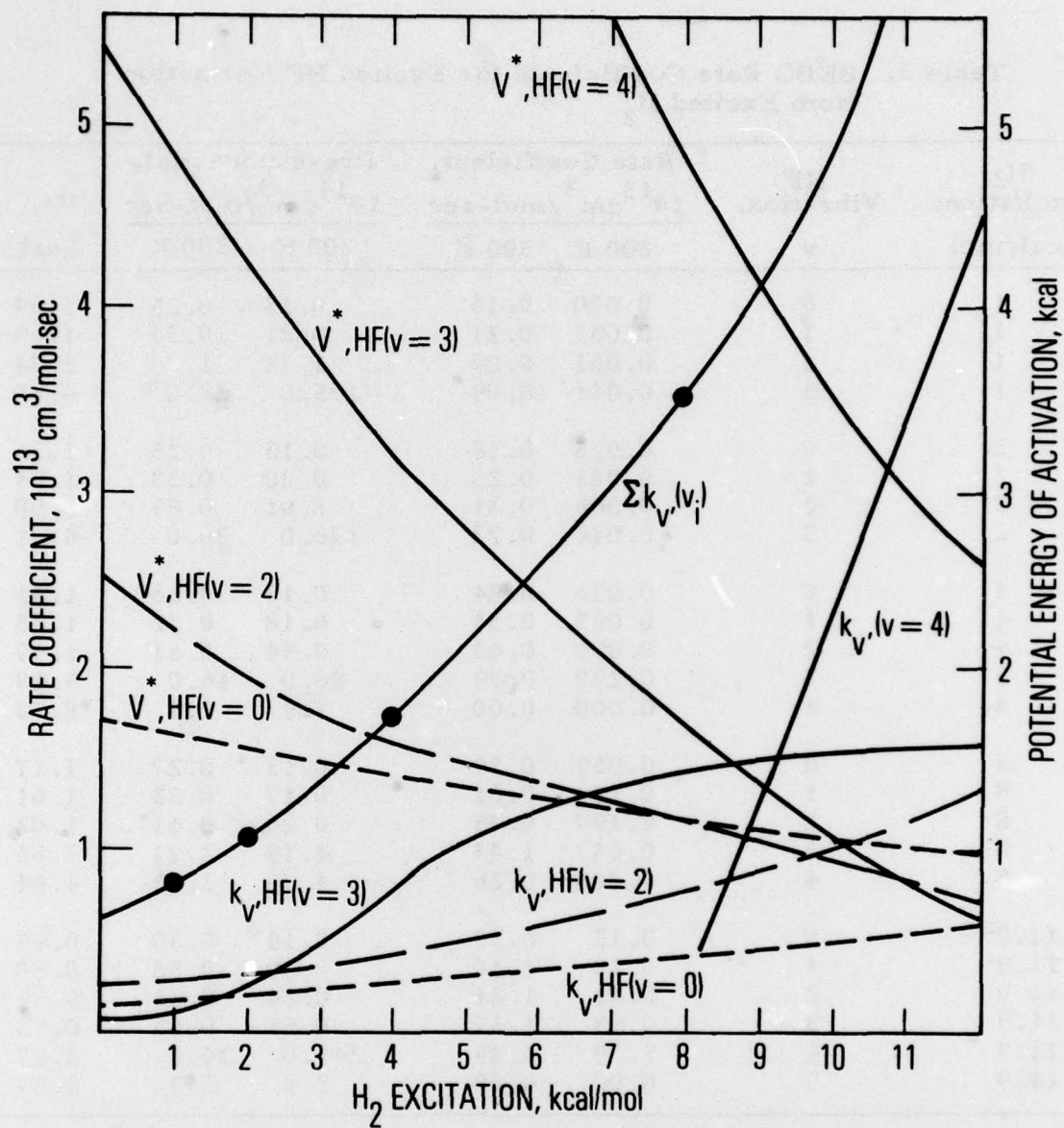


Fig. 1. Effect of Excitation of Reactant H<sub>2</sub> on Kinetics of HF Formation

only with ground-state reactants and products. Consequently, BEBO results were confined to the intercept (Fig. 1) of the HF( $v = 0$ ) line with the ordinate axis, corresponding to ground-state reactant. Those results did not provide the overall rate coefficients for reactions in which excited products were formed. Because of the abundance of computed values for kinetic parameters obtainable when the BEBO method is extended to excited states, it is planned to make an extensive series of BEBO calculations for excited-state atom-transfer reactions that are exothermic or thermonutral.

Table 2 indicates that even though  $V^*$  increases as the vibrational level of the HF product rises from  $V = 0$  to  $V = 2$ , the computed rate coefficient increases to produce inversions. As pointed out earlier,  $k_v$  is calculated as the product of  $\exp(-V^*/RT)$  with the pre-exponential factor  $B$ . Consequently, it is apparent from the results in Table 2 that the increase in  $k_v$  for  $v = 2$  compared with  $k_v$  for  $v = 0$  or  $1$  arises because the increase in  $B$  for  $v = 2$  is sufficient to outweigh the effect of the larger  $V^*$  for  $v = 2$ . Therefore, the prediction by BEBO of these HF inversions arises from the dependence of  $B$  on the  $v$  of the HF product. In order to understand the source of the predicted magnitude of inversions, it was necessary to evaluate the relative importance of each of the factors determining the dependence of  $B$  on  $v$ . The value of  $B$  is dependent on a large number of factors [summarized in equation (4)] obtained on the basis of a small vibration analysis of the triatomic state and the diatomic reactant.<sup>5</sup>

$$B = 1.81 \times 10^{13} A \frac{Q_1 Q_3}{Q_{H_2}} \frac{r_1^2 r_2^2 W_v}{R_{H_2}^2} \frac{l_{11} l_{22} l^2 \phi}{l_{H_2}} \text{ cm}^3/\text{mol-sec} \quad (4)$$

where  $A$  is a constant that is dependent on such molecular parameters as electronic degeneracy and symmetry number;<sup>5</sup>  $Q_1$  is the quantum contribution factor for stretching vibration in the transition state;  $Q_3$  is the quantum contribution factor for bending vibration in the transition state;  $Q_{H_2}$  is the

quantum contribution factor for the vibration of the reactant  $H_2$ ;  $r_1$  is the interatomic distance for the breaking bond in the transition state;  $r_2$  is the corresponding distance for the new bond;  $R_{H_2}$  is the bond length of  $H_2$ ;  $W$  is the reciprocal of the square root of the absolute value of the quantity  $[1 - (F_{12}^2/F_{11}F_{22})]$ , where  $F_{12}$ ,  $F_{11}$ , and  $F_{22}$  are the force constants for Wilson's  $F$  matrix as defined in Ref. 5;  $v$  is an algebraically intricate function of  $F_{12}$ ,  $F_{11}$ ,  $F_{22}$ , and the atomic masses,<sup>5</sup> and the  $l$ 's are the corresponding vibrational amplitudes for stretching and bending. The dependence of these factors on the value of  $v$  was examined to determine which factors were most important in producing the aforementioned increase in  $B$  as  $v$  for  $HF$  rose from 0 to 3. The significant results are summarized in Table 4. An examination of the effect of each factor (by use of the computer program printout) revealed that the outstanding factor that influenced the increase in  $B$  as a function of  $v$  was the quantum contribution  $Q_1$  to the stretching vibration of the transition state (e. g.,  $Q_1$  increased from 0.36 for  $HF(v = 1)$  to 17 for  $HF(v = 2)$ ). Other factors had comparatively little effect on  $B$ , as illustrated in Table 4 by the quantum factor  $Q_3$  for the bending vibration of  $H \cdots H \cdots F$ .

The important stretching quantum factor  $Q_1$  is calculated from the exponential expression

$$Q_1 = \frac{w e^{-w/2}}{1 - e^{-w}} \quad (5)$$

where  $w$  is proportional to the stretching frequency of the transition state. In order to determine which molecular properties were of particular importance in obtaining the value of  $w$  and therefore of  $Q_1$  and  $B$ , the factors involved in computing  $w$  were studied. It was observed that, for reactions in which an  $H$  or  $D$  atom is transferred, the interaction force constant  $F_{12}$  in the transition state is the most significant quantity that affects the computed value of  $w$ . ( $F_{12}$  determines the interaction caused by distortion of one bond.)



Table 4. Components of Pre-exponential Term<sup>a</sup>

HF Vibrational Level, v	Pre- exponential, B, 10 <sup>14</sup> cm <sup>3</sup> /mol-sec	Stretching Factor, Q <sub>1</sub>	Bending Factor, Q <sub>3</sub>	Interaction Force Constant, F <sub>12</sub>	Bond Order, m* at V*	Bond Order Factor, μ*	F - F', F*
0	0.13	0.14	0.50	0.47	0.08	0.086	5.5
1	0.24	0.36	0.49	0.70	0.12	0.134	5.2
2	3.06	17.0	0.42	1.24	0.26	0.313	4.0
3	190.0	2480.0	0.45	2.45	0.58	0.478	5.1
4	3.2	10.0	0.50	0.18	0.97	0.035	5.1

<sup>a</sup>For H<sub>2</sub> + F ⇌ H + HF(v = 0, 1, 2, 3, 4) at 200 K



Because of the exponential nature of the dependence of  $Q_1$  on  $w$ , relatively small changes in  $F_{12}$  can produce large changes in  $Q_1$  and  $B$ , as indicated in Table 4.

The search for the major factors that affect  $k_v$ ,  $B$ , and  $Q_1$  as a function of  $v$  was continued by studying the factors that determine the magnitude of  $F_{12}$ , which in turn is the product of two quantities,  $\mu^*$  and  $F^*$ :

$$\mu^* = \frac{m^{*2} - m^*}{2m^* - 2m^{*2} - 1} \quad \text{and} \quad F^* = F_\sigma - F_\rho \quad (6)$$

where  $m$  is the bond order of  $H \cdots F$  (in the transition state at  $V^*$ ).  $F_\sigma$  and  $F_\rho$  are transition-state force constants (Ref. 5, p. 341). As indicated in Table 4, the dependence of  $F^*$  on  $v$  is relatively unimportant, but the dependence of  $\mu^*$  on  $v$  is significant, much as the dependence on  $v$  of  $F_{12}$ ,  $Q_1$ , and  $B$  was found to be important for generating computed values of  $k_v$  that predicted HF inversions. Thus, where  $\mu^*$  in Table 4 is highest (at  $v = 3$ ),  $B$ ,  $Q_1$ , and  $F_{12}$  are also high.

It was mentioned in connection with Table 3 and Fig. 1 that excitation of reactant  $H_2$  tends to increase  $k_v$  by lowering  $V^*$ . It should be pointed out that excitation of  $H_2$  can also increase  $k_v$  for production of excited HF as a consequence of raising  $\mu^*$ . Because of the symmetry resulting from the relationship  $m + n = 1$  (given in Section II),  $\mu^*$  is maximized at  $m^* = 0.5$  (Table 5). Inasmuch as  $k_v$  and  $B$  increase when  $\mu^*$  increases, the highest values of  $k_v$  and  $B$  can be expected (if other factors are equal) when  $m^*$  is nearest 0.5. It has been shown in many previous hydrogen-transfer reaction BEBO computations,<sup>4-7</sup> that  $m^* = 0.5$  when the potential energy for dissociation of the reactant equals the potential energy of formation of the diatomic product. For the chemical laser reaction

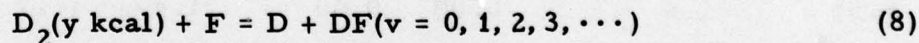


Table 5. Dependence of Bond Order Factor  $\mu^*$  on the Value of  $m^*$

$m^*$ or 1- $m^*$	$\mu^*$	$m^*$ or 1- $m^*$	$\mu^*$
0.50	0.500	0.20	0.235
0.42	0.478	0.167	0.193
0.40	0.462	0.14	0.160
0.375	0.440	0.12	0.134
0.333	0.400	0.10	0.110
0.30	0.365	0.08	0.086
0.26	0.313	0.05	0.053
0.25	0.300	0.01	0.01

the potential energy for dissociation of ground-state  $H_2$  is about 1.2 kcal higher than the potential energy of formation of  $HF(v = 3)$ . As indicated in Table 2, the BEBO rate coefficient for generating the desired  $HF(v = 3)$  lasing species from ground-state  $H_2$  reactant is less than that for  $HF(v = 2)$  because the pre-exponential factor is not high enough to overcome the effect of a relatively high value of  $V^*$  for  $HF(v = 3)$ . By the use of  $H_2$  reactant excited to about 1.2 kcal in the chemical laser,  $\mu^*$  could, however, be maximized at  $m^* = 0.5$  to increase  $k_v$  for  $HF(v = 3)$  relative to that for unexcited  $H_2$  reactant. The  $k_v$ 's of  $HF(v = 3)$  in Table 3 for  $H_2$  excited to 1 and 2 kcal/mol are consistent with this expectation.

Results are summarized in Table 6 for BEBO computations pertinent to the reaction



where  $y$  kcal, the excitation of reactant  $D_2$ , equals 0, 1, 2, 4, 8.56, or 16.80. The latter two values correspond to the first and second vibrational levels of  $D_2$ , respectively, with no rotational excitation.<sup>14</sup> The overall BEBO rate



Table 6. BEBO Results for Excited DF Formation from Ground-State and Excited D<sub>2</sub>

D <sub>2</sub> Excitation, kcal/mol	DF Vibration, v	Rate Coefficient, 10 <sup>12</sup> cm <sup>3</sup> /mol-sec		Pre-exponential, 10 <sup>14</sup> cm <sup>3</sup> /mol-sec		V*, kcal/mol
		200 K	300 K	200 K	300 K	
0	0	0.13	0.98	0.10	0.18	1.73
0	1	0.16	1.08	0.13	0.21	1.76
0	2	0.16	1.00	0.28	0.32	2.06
0	3	0.11	0.74	2.23	1.17	3.02
0	4	0.06	0.03	12.42	3.72	5.54
1	0	0.17	1.19	0.10	0.18	1.63
1	1	0.21	1.32	0.13	0.20	1.63
1	2	0.21	1.25	0.35	0.28	1.86
1	3	0.17	0.98	1.31	0.84	2.65
1	4	0.04	0.21	13.20	3.85	4.88
2	0	0.21	1.36	0.10	0.18	1.55
2	1	0.27	1.59	0.12	0.20	1.52
2	2	0.28	1.53	0.20	0.26	1.69
2	3	0.25	1.30	0.88	0.65	2.34
2	4	0.08	0.48	12.83	3.77	4.29
4	0	0.31	1.85	0.11	0.19	1.40
4	1	0.43	2.24	0.12	0.21	1.33
4	2	0.48	2.31	0.16	0.24	1.40
4	3	0.55	2.62	0.42	0.42	1.81
4	4	0.23	1.22	8.00	2.76	3.23
8.56 <sup>a</sup>	0	0.72	3.55	0.12	0.24	1.13
8.56	1	1.08	4.57	0.13	0.25	1.00
8.56	2	1.39	5.19	0.15	0.25	0.95
8.56	3	1.49	5.39	0.20	0.28	1.03
8.56	4	1.71	4.95	0.82	0.65	1.54
8.56	5	0.22	1.21	16.16	4.56	3.54
8.56	6	0.00	0.00	1.49	1.17	7.97
16.80 <sup>a</sup>	0	1.93	7.29	0.15	0.28	0.80
16.80	1	3.45	11.20	0.17	0.33	0.65
16.80	2	5.70	16.38	0.21	0.39	0.52
16.80	3	8.69	22.73	0.26	0.47	0.43
16.80	4	9.03	21.46	0.24	0.42	0.39
16.80	5	8.83	17.75	0.31	0.41	0.50
16.80	6	22.59	27.29	17.24	4.91	1.72
16.80	7	0.00	0.00	1.24	1.19	6.14

<sup>a</sup>The first and second vibrational levels of D<sub>2</sub> are excited by 8.56 and 16.80 kcal/mol, respectively.<sup>14</sup>



coefficient for the reaction of ground-state  $D_2$  at 300 K (Table 6) to produce  $DF(v = 0, 1, 2, 3, \text{ and } 4)$  is  $3.8 \times 10^{12} \text{ cm}^3/\text{mol-sec}$ . This result is in reasonable agreement with the rate coefficient of  $(7.6 \pm 4) \times 10^{12} \text{ cm}^3/\text{mol-sec}$  at 300 K obtained from an experimentally derived<sup>16, 9</sup> rate coefficient  $k_8 = (1.5 \pm 0.5) \times 10^{14} \exp(-1970/RT)$ ,  $\text{cm}^3/\text{mol-sec}$ . The mean BEBO potential energy of activation is computed to be 2.1 kcal/mol for the ground-state  $D_2$  reactions when  $V^*$  for  $HF(v = 0, 1, 2, \dots)$  production is weighted in Table 6 in proportion to the corresponding rate coefficients. Application of a tunneling correction to the BEBO calculation would be expected to raise the computed  $k_8$ , although tunneling factors for deuterium normally are lower than for hydrogen.<sup>15</sup> The ratio of the BEBO overall  $k_v$  at 300 K for ground-state  $H_2$  (Table 2) to that for ground-state  $D_2$  (Table 6) is 1.6, in satisfactory agreement with the corresponding ratio of 1.8 to 2.0 given in Ref. 9.

The inversions predicted by the BEBO method for  $DF$  (Table 6) are generally weaker than those predicted for  $HF$ . The BEBO rate coefficients in Table 6 indicate inversions of  $DF(v = 3)$  relative to  $DF(v = 2)$  only when the excitation of  $D_2$  is more than 2 kcal/mol. Although the BEBO rate coefficients for  $DF(v = 4)$  agree with experiment<sup>16</sup> [they are smaller than for  $DF(v = 3)$ ], they are too small compared with those for  $DF(v = 3)$ , except when the excitation for  $D_2$  reactant (Table 6) is larger than 1 kcal. The effect of  $D_2$  excitation in favoring an increase in BEBO rate coefficients, particularly for higher vibrational quantum numbers of the  $DF$  reaction product, is similar to the effect of  $H_2$  excitation (Table 3) in favoring larger BEBO rate coefficients for more highly excited  $HF$  product. Thus, in Table 6, the highest BEBO rate coefficients when  $D_2$  is excited to 16.8 kcal are for  $DF(v = 6)$ .

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